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Computer simulation study of oxygen migration in $YBa_2Cu_3O_7$

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Abstract. Atomistic simulation techniques have been applied to orthorhombic $YBa_2Cu_3O_7$ in order to calculate the energetics of oxygen migration. The techniques are based on energy minimization methods and the Mott–Littleton methodology, which effectively treat lattice relaxation around defects. A variety of migration mechanisms are considered including vacancy, direct interstitial and interstitialcy mechanisms. The results support the models in which ionic diffusion is attributed to the mobility of oxygen vacancies. High energy barriers are calculated for migration of oxygen interstitials. We find that an interlayer vacancy mechanism involving O(1) chain and O(4) apical sites is the most favourable migration mechanism.

1. Introduction

Numerous studies have shown that the properties of the $YBa_2Cu_3O_{7-x}$ superconductor are strongly dependent upon the oxygen content. For instance, deviations in the oxygen stoichiometry affect the electronic behaviour of the normal state, the crystallographic structure and the superconducting transition temperature in the range 90 K (when $x \approx 0$) to 0 K (when $x = 1.0$). It is therefore important to study and understand the behaviour of oxygen ions and associated point defects in this compound.

The structure of $YBa_2Cu_3O_{7-x}$ is now well established as an oxygen-deficient trilayer perovskite [1–3], which as a 90 K superconductor is orthorhombic with four occupied oxygen sites, shown in figure 1. It is worth noting that non-stoichiometry and related defect chemistry is not unusual in perovskite or perovskite-like compounds (see, for example, the review by Smyth [4]). Powder neutron diffraction [5–8] and x-ray absorption fine structure (XAFS) experiments [9] of $YBa_2Cu_3O_{7-x}$ have shown that decreasing the oxygen content results in progressive depopulation of oxygen from the O(1) chain sites, with no detectable change in occupancy of the O(2) and O(3) sites in the Cu(2)–O plane. For samples quenched from high temperature there is also evidence for additional vacancies on the bridging O(4) oxygen site between Cu(1) and Cu(2) [7, 8, 10, 11]. However, it is not certain whether the O(4) vacancies are associated with alternate Cu(1)–O chains or are randomly distributed. In any case, oxygen vacancies are thought to be present in order to charge-compensate the change in Cu valence as $YBa_2Cu_3O_{7-x}$ is reduced. We note that the possibility of variable cation valence, resulting in the creation of charge-compensating defects, is typical of non-stoichiometric compounds.

The importance of oxygen stoichiometry in $YBa_2Cu_3O_{7-x}$ has resulted in a number of studies of oxygen diffusion by a variety of techniques. Early experimental work by Glowacki *et al* [12] using differential scanning calorimetry obtained an activation energy of $E_a = 1.5$–1.6 eV. From internal friction measurements, Xie *et al* [13] interpreted their data in terms of diffusional jumps in the basal planes between sites O(5) and O(1), and obtained an activation energy of $E_a = 1.03$ eV. Zhang *et al* [13] have also reported internal friction measurements as a function of temperature, and measured an activation energy of $E_a = 1.12$ eV for

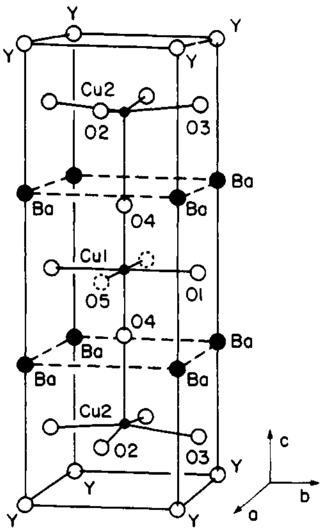

Figure 1. Unit cell of orthorhombic $YBa_2Cu_3O_7$.

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the superconducting orthorhombic phase. In particular, they propose that the transport properties are associated with either an ordering diffusion process between layers or an order/disorder diffusion process in the Cu(2) plane. Tu *et al* [15] determined activation energies by *in situ* resistivity measurements, with $E_a = 0.5$ eV at $x = 0.38$ and $E_a = 1.3$ eV at $x \approx 0$, in the temperature range of 250–500 °C. According to these authors, the former corresponds to the activation energy of motion of oxygen and the latter to the diffusion of oxygen, which consists of energies of formation and motion. They also postulated that oxygen diffusion is mediated by a vacancy mechanism. From ionic conductivity studies Carrillo-Cabrera *et al* [16] reported an activation energy of 2.2 ± 0.1 eV, from which they derived a migration enthalpy of 1.0 ± 0.1 eV. On the basis of crystallographic arguments, they assumed that oxygen migration would mainly occur within the Cu(1) basal plane by a vacancy mechanism. On the other hand, recent thermogravimetric studies of chemical diffusion [17] viewed oxygen diffusion to proceed via an interstitial-like mechanism in the basal plane and measured an activation energy of 1.38 eV at $x = 0$. From calculations based on effective medium theory, Ronay and Norlander [18] also attributed the observed conductivity to an interstitial mechanism along the *b*-axis 'tunnel'. More recently, measurements of oxygen tracer diffusion by Rothman *et al* [19] indicated that diffusion is highly anisotropic with diffusion in the *ab* plane much faster than along the *c*-axis. Furthermore they concluded that the diffusion coefficient for the faster component may be described by a single activation energy of 0.97 ± 0.03 eV over a wide range of stoichiometry, in contrast with the results of Tu *et al* [15]. Oxygen diffusion in tetragonal $YBa_2Cu_3O_{7-x}$ has also been studied by *in situ* resistivity measurements [20], which suggest a process controlled by a single mechanism having an activation energy of $E_a = 0.40 \pm 0.05$ eV.

The activation energies reported by the various studies thus show significant scatter. This may be partly attributed to differences in experimental conditions. An additional complication is the fact that $YBa_2Cu_3O_{7-x}$ is a mixed conductor in which charge may be transported by both electronic and ionic carriers. Despite the range of studies on oxygen diffusion, the precise nature of the ion transport mechanism is still uncertain. Unfortunately, the information provided by experimental diffusion studies cannot always be deconvoluted sufficiently to identify the atomic mechanisms controlling mass transport, particularly for complex structures.

In an attempt to clarify this situation we have undertaken a study of oxygen transport in orthorhombic $YBa_2Cu_3O_7$ using computer simulation techniques, which are well suited to probing defect structures and migration mechanisms at the atomic level.

Following the success of simulation methods in calculating experimentally measured defect parameters for a wide range of polar solids, including transition metal oxides [21–24], these techniques have been applied to the high T_c superconducting oxides La_2CuO_4 [25–28], $YBa_2Cu_3O_7$ [29, 30] and the Bismuth cuprates [31]. The present study extends our previous work on defects and dopants in $YBa_2Cu_3O_7$ by examining the energetics of a number of possible vacancy and interstitial mechanisms for oxygen migration.

2. Theoretical methods

The atomistic simulations are based on the Mott–Littleton methodology for non-cubic crystals programmed in the CASCADE code [32]. The present account of these widely used techniques will, however, be brief since detailed reviews are given by Catlow and Mackrodt [33] and Catlow [34].

An essential feature of the defect calculations is the treatment of lattice relaxation about the defect centre. Indeed, owing to the strong interaction between the migrating ion and the polar lattice the relaxation energies will be large. The Mott–Littleton approach is to partition the crystal lattice into two regions so that ions in the central inner region (I) surrounding the defect, where the forces exerted by the defect are strong, are equilibrated explicitly; whereas the remainder of the crystal is treated more approximately as a dielectric continuum. The simulation of the inner region employs efficient energy-minimization methods that make use of first and second derivatives of the energy function with respect to atomic coordinates. For the results presented here 225 ions were used in region I, which is sufficiently large for the computed energy to be no longer sensitive to an increase in region size.

The effective potentials describing the interatomic forces are represented by ionic, pair-wise potentials of the form

$$\phi_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \qquad (1)$$

which is comprised of the long-range Coulomb term and an analytical function of the Buckingham form to represent short-range interactions. Note that the use of the Born model does not necessarily imply that the electron density distribution corresponds to a fully ionic description, and that the general validity of the model is assessed mainly by its ability to reproduce observed crystal properties [35].

Ionic polarization is described by the shell model [36], which has been shown to simulate effectively both dielectric and elastic properties. The shell model also allows the coupling between short-range repulsive forces and polarizability: an important physical feature whose omission from earlier point-dipole models resulted in serious problems in simulating crystalline solids.

In the present examination of oxygen migration, the same two-body potentials for $YBa_2Cu_3O_7$ are used as in our previous simulation studies [29, 30], in which all the Cu ions are considered in the 2+ charge state, with the hole uniformly distributed on the O(1) and O(4) oxygens. The potentials were derived by a standard empirical procedure that gives a good representation of the potential at or near equilibrium interatomic separations. However, for certain defect centre configurations where the interatomic separations may deviate from the perfect lattice values, the validity of the analytical form describing the potential is assumed. The assumptions will probably lead to some errors in the calculated defect energies; their magnitudes are, however, small compared with those that may arise from other approximations in our models. In fact, numerous studies using empirical potentials have successfully calculated defect migration energies in which ions are displaced from perfect lattice positions. It is worth emphasizing that the potential model for $YBa_2Cu_3O_7$ correctly reproduced the observed orthorhombic structure and predicted the O(1) oxygen chain site as the most favourable vacancy site in agreement with experiment. Full details of the potential parameters and computed crystal properties are given elsewhere [29].

Finally in this section, we note that Baetzold [37] recently derived three new sets of potentials for $YBa_2Cu_3O_7$ by empirical fitting to the structure and experimental elastic constants. The preferred model, which includes three-body angle-dependent terms, was used to investigate defects, bipolaron formation and oxygen transport in the oxide. The present study complements and extends this work by using the original two-body potential model to examine migration mechanisms previously not considered.

3. Results and discussion

For the complex structure of $YBa_2Cu_3O_7$ there are a number of different pathways, each with its individual frequency factor for migration. Thus, it is not easy deciding which are the most likely paths.

We have identified various possible defect mechanisms for oxygen migration between neighbouring sites, which are illustrated in figures 2 to 5. Of the nine

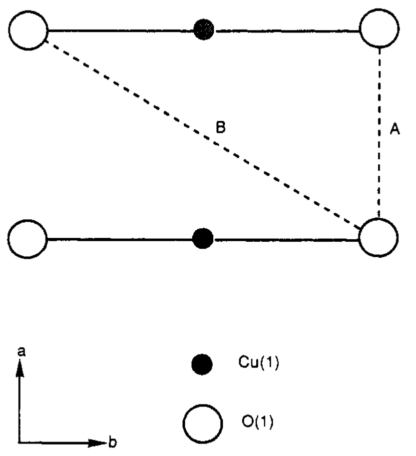

Figure 2. Intrachain vacancy migration mechanisms.

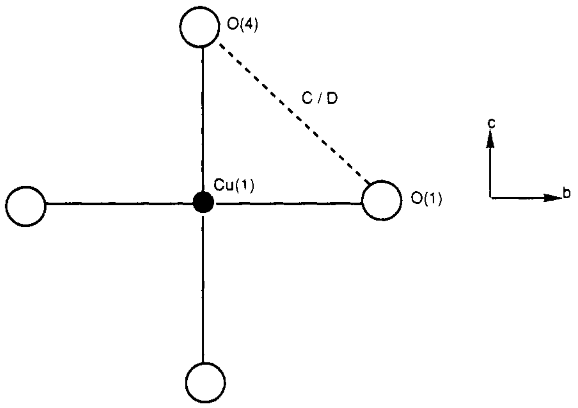

Figure 3. Interlayer vacancy migration mechanisms: C and D involve O(1) chain and O(4) apical oxygen vacancies respectively.

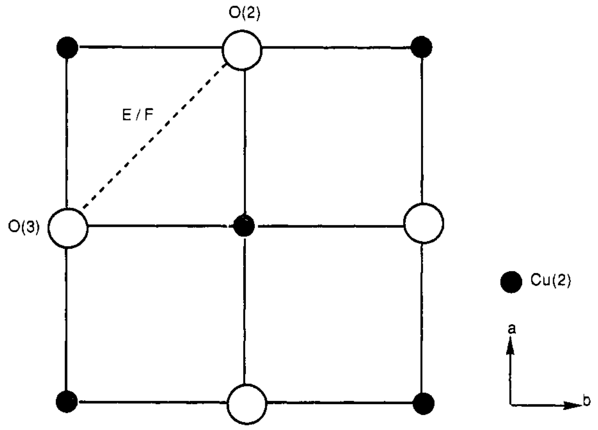

Figure 4. Intraplanar vacancy migration mechanisms: E and F relate to O(2) and O(3) oxygen vacancies respectively.

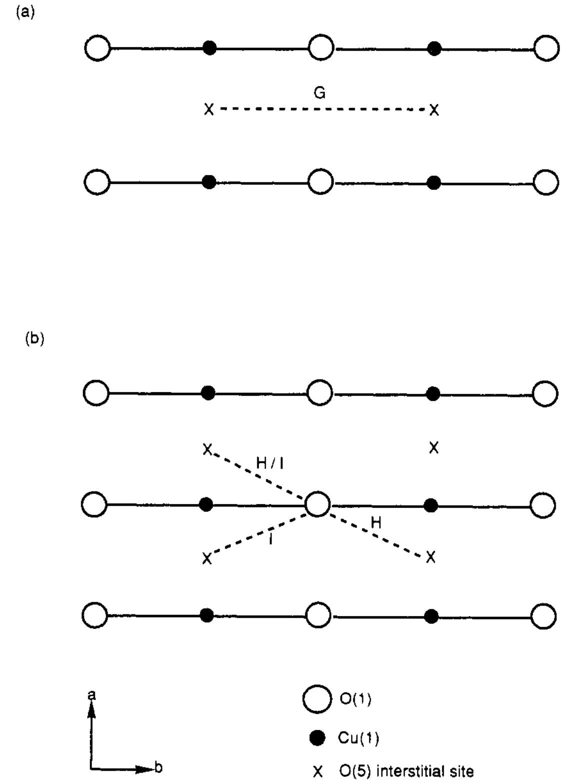

Figure 5. Oxygen interstitial migration: (*a*) direct interstitial mechanism; (*b*) interstitialcy mechanisms.

mechanisms considered, six involve oxygen vacancies (denoted by A to F) and the other three (G, H and I) are concerned with oxygen interstitials. Mechanisms A and B are associated with intrachain migration, with B involving a diagonal jump through the O(5) interstitial position (figure 2). Mechanisms C and D involve out-of-plane (or 'interlayer') migration between O(1) and O(4) sites (figure 3). Mechanisms E and F relate to jumps in the Cu(2)–O plane (figure 4), and would effect diffusion only within the *ab* plane. For interstitial migration, three mechanisms were considered involving the interstitial position at ($\frac{1}{2}$ 0 0): a direct mechanism along the [$\frac{1}{2}$ *b* O] tunnel (figure 5(*a*)), and two concerted or 'interstitialcy' jumps in which the migrating ion displaces a neighbouring lattice ion into the adjacent interstitial site (figure 6). The latter involve the correlated motion of ion pairs in a collinear (H) or non-collinear (I) fashion. The importance of such interstitialcy mechanisms has been shown in earlier work on fluorite-structured materials. Note that as a structural aspect we view the ($\frac{1}{2}$ 0 0) position as an interstitial site and not a vacancy, since it is a normally unoccupied site in $YBa_2Cu_3O_7$.

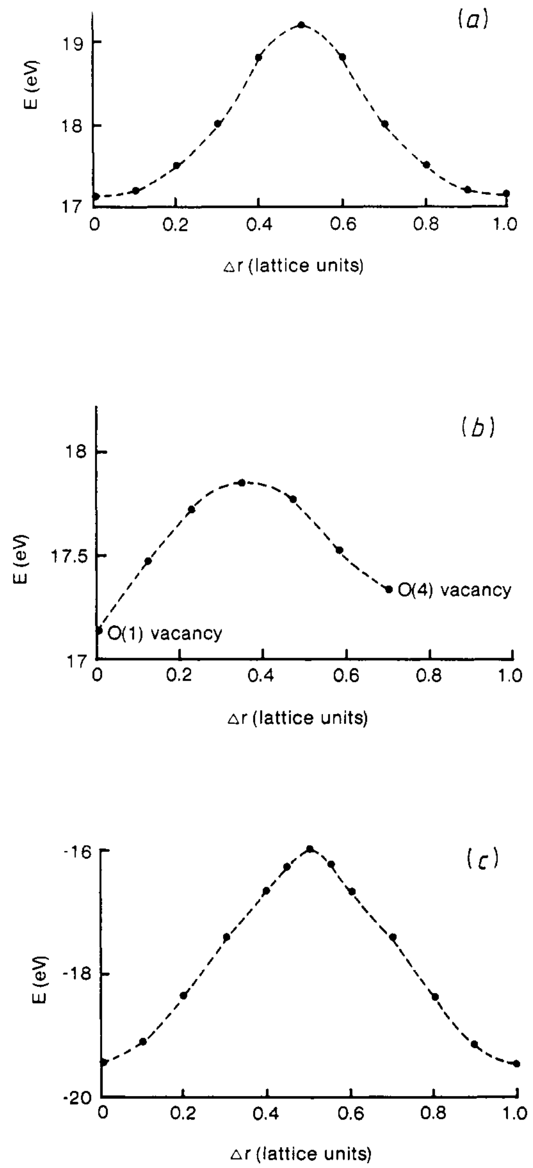

Figure 6. Potential energy profiles of migration paths: (*a*) intrachain A; (*b*) interlayer C and D; (*c*) direct intersitial G.

Owing to the number of possible migration mechanisms, an unambiguous interpretation of any diffusion data can be difficult. Here, reliable values of migration energetics from theoretical methods, which are able to examine diffusion atomistically, are particularly useful.

The energy barriers to migration are evaluated by calculating the defect energy of the migrating ion at positions along the diffusion path, and allowing the remainder of the lattice to relax in the energy minimization procedure. In this way it is possible to map out the energy profile and to identify the position of highest potential energy (i.e. saddle-point) that the ion must overcome between the two equilibrium sites. The resulting energy profile for mechanisms A, C, D and G are shown in figure 6. Considering that the saddle-point for mechanisms C and D is the same, the calculated activation energies depend on the relative stabilities of their ground-state configurations, i.e. their vacancy formation energies. This is also the case for the intraplanar mechanisms E and F.

This energy profile procedure rests upon the validity of the conventional hopping model of ion transport, where motion is effected by distinct, discrete events or 'hops' of atoms. In general, the most important condition, namely that the activation enthalphy $E_a \gg kT$, is normally satisfied [34]. Thus energy profiles were calculated for each of the nine mechanisms in $YBa_2Cu_3O_7$. The resulting activation energies for vacancy and interstitial mechanisms are reported in tables 1 and 2, respectively.

Examination of the results shows that out-of-plane vacancy migration emerges as the lowest energy path. The corresponding mechanisms, C and D, are associated with O(1) and O(4) vacancies and calculated migration energies of 0.72 eV and 0.51 eV, respectively. This type of interlayer mechanism is thus favoured over the other intralayer, intrachain and interstitial mechanisms considered. Interestingly, the corresponding O–O distance for intrachain diffusion by mechanism A is 3.82 Å, whereas for interlayer diffusion the distance is 2.68 Å.

Table 1. Calculated migration energies for oxygen vacancy mechanisms.

Mechanism	Vacancy site	E_m (eV)
Intrachain		
A	O(1)	2.09
B	O(1)	2.73
Interlayer		
C	O(1)	0.72
D	O(4)	0.51
Intraplanar		
E	O(2)	1.20
F	O(3)	1.34

Table 2. Calculated migration energies for oxygen interstitial mechanisms.

Mechanism	Direction	E_m (eV)
Direct		
G	along *b*-axis	3.40
Interstitialcy		
H	collinear	2.16
I	non-collinear	5.40

Since the saddle-point configuration is identical for both C and D, the diffusion of vacancies will also be controlled by their formation energetics. As noted earlier, neutron diffraction studies have demonstrated that oxygen vacancies form preferentially on the O(1) sublattice. Furthermore, simulation studies [29] have calculated vacancy formation energies for each of the four non-equivalent oxygens, finding O(1) the most favourable site. These studies suggest that the concentration of vacancies will be greatest at the O(1) chain site and therefore most likely to be responsible for oxygen transport. Thus we predict that diffusion mediated by mechanism C would dominate, with a migration energy of $E_m = 0.72$ eV. Nevertheless, there is some evidence from diffraction experiments for additional vacancies on the O(4) apical site, which may result in migration via mechanism D with a slightly lower migration energy of 0.51 eV. Based upon similar arguments mechanisms involving diffusion on the Cu(2)–O plane seem unlikely, since the concentration of vacancies on the O(2)/O(3) sublattice will be negligible.

Oxygen diffusion is therefore predicted to be dominated by vacancies, but restricted to migration between the O(1) and O(4) layers in a zig-zag fashion. Hence, long-range diffusion will be governed by transport essentially in the *ab* plane. In view of this type of motion and the layered nature of the structure, the observed anisotropic ion diffusion is not surprising.

From their discussion on relaxation processes, Zhang *et al* [14] suggested the most likely mechanisms to be intralayer vacancy migration on the Cu(2)–O plane and interlayer vacancy migration between O(1) and O(4) layers. The latter process would be consistent with our results. Moreover, the calculated migration energies are in accord with an observed value of $E_a = 0.5$ eV, which Tu *et al* [15] associated with an activation energy for migration. As already indicated, however, there are significant variations in the experimental activation energies which might reflect differences in processing conditions and oxygen content, so that direct comparison with theory may not always be meaningful.

It is clear from examination of table 2 that both direct and interstitialcy interstitial migration have high migration energies, which implies that they would not be expected to contribute to the ionic conductivity in this compound. We note that a discussion of interstitial migration has been given by Ronay and Norlander [18]—from a theoretical investigation they propose that there is no potential energy barrier for oxygen interstitial motion in the *b* direction. However, by analysing the structural dimensions along the $[\frac{1}{2}\ b\ 0]$ tunnel, Alario-Franco *et al* [38] suggested that oxygen interstitial migration would be restricted by the rhombus formed by two Ba ions and two O(1) ions. Our calculations are consistent with this view, and indeed the large barrier height evident in the computed energy profile (figure 6(*c*)) is due to the increase in repulsive interactions as the migrating ion moves nearer the saddle-point.

We should add that our results are in contrast with the conclusions reached from a recent simulation study of Baetzold [37], which favours vacancy mechanisms on the Cu(2)–O plane, although the interlayer mechanism was not considered. Our calculations clearly show that the intraplanar mechanisms have relatively high activation energies and therefore would not dominate the diffusion properties. Such differences may be attributed partly to differences in the form of the short-range Cu–O potentials, particularly at the off-centre saddle-point positions. The potentials taken from [29] are generally more repulsive, which leads to slightly increased migration energies. Nevertheless, from the simulations of Baetzold [37] interstitial migration was found to have prohibitive energy barriers in accord with our calculations.

4. Conclusions

It has been shown that atomistic simulation methods based on shell-model potentials provide a useful way of investigating oxygen migration in $YBa_2Cu_3O_7$. Indeed, we are able to examine mechanisms previously ignored by two-dimensional models which assume that oxygen diffuses only in the *ab* plane. Two main conclusions emerge from our discussion. First, the calculations find migration involving oxygen vacancies energetically favourable, with high energy barriers to interstitial migration. The results thus support models in which mobility of oxygen vacancies is responsible for conduction.

Second, vacancies at the O(1) oxygen chain sites are predicted to be the most mobile species and shown to diffuse through the bulk by an interlayer mechanism involving adjacent O(4) oxygen ions. This is consistent with diffraction experiments which find that the concentration of oxygen vacancies is predominantly at the chain position. While there may remain some uncertainties in the calculated migration energies, we consider the dominant vacancy mechanism to be a plausible model for diffusion in this oxide, at least on a qualitative level.

Finally, we note that there is still uncertainty as to the degree of association or ordering of oxygen vacancies in the oxide structure, which could clearly influence the ion transport properties. This topic is currently under investigation.

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